

Draft Final Report

submitted to

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER, ALABAMA 35812**

June 20, 1997

for Contract NAS8 - 38609

Delivery Order 165

entitled

ZBLAN Fiber Phase B Study

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1.0 Introduction

The structure of glass systems has been studied extensively over the last fifty years, developing a fairly good foundation for its properties. Unfortunately most of that activity has been devoted to systems based on silica, which behave in a generally consistent framework.[1] Glasses prepared from systems other than silica, can possess useful characteristics for applications as optical devices; however, the limiting factors imposed on the usage of these materials is normally due to instabilities which have not been resolved in producing these routinely. For instance, the heavy metal fluoride glasses (HMFG) possess unique infra-red transmission properties, but producing a formulation that behaves consistently still presents a problem after over 20 years of research and development. HMFG and other unstable systems present an entirely different perspective on the structure and behavior of glass. Although a tremendous amount of research activity was pushed forward in the 1980's to develop the highest transmitting infra-red optical fiber available on the world market, we still do not have a good understanding of the HMGL structure and how this structure provides the observed characteristics of the various materials currently used for optical fiber applications. The inclusion of many components into the mixture did provide an optical glass with fairly good transmission characteristics with some devitrification problems. ZBLAN is the fluorozirconate composition that has evolved into commercial offerings as an optical fiber with reasonable results.

It has been the intent of this study to utilize microgravity processing of HMGL materials to improve our understanding of the microstructure and processing characteristics for ZBLAN glass. Prior work with fiber annealing experiments of commercially provided ZBLAN fiber indicated that nucleation phenomena are reduced in reduced gravity. These observations were performed separately by two different groups independently and provide an incentive to perform further comparisons between fluoro-zirconate compositions processed on the ground and in the microgravity environment of space. Methodologies to determine quantitative nucleation and growth parameters is necessary to evaluate the effect of gravity on the processing of these materials and to assist in the understanding of how these glasses differ from the more traditional silica glasses.

The experiments performed here have been oriented toward the design of a flight experiment to determine distribution and size of nucleation sites over time using laser scattering from particles nucleated from glass melts above the glass transition and nucleation. Comparison with reported data from previous fluorozirconate experiments can then provide insight into mechanisms for nucleation and growth in these materials. Laser light scattering apparatus does already exist and may be useful in performing this experiment in space. Also the experiment, once fully conceptualized, can very easily be performed as a glove box experiment in space.

2.0 Experimental Objectives

The objective of this work was to measure the nucleation and growth kinetics of fluorozirconate glasses using laser attenuation techniques. The fluorozirconate glasses constitute a grouping of fluorides containing zirconium, barium, lanthanum, aluminum, sodium, cadmium, lead and other elements which provide very useful properties as optical glass, but are very susceptible to devitrification during processing. The of optical fibers made from these materials possess excellent transmission characteristics in the infrared region. Examples of these materials which have been studied extensively in 1 g include ZBLAN (fluorides of zirconium, barium, lanthanum, aluminum, and sodium) and CLAP (cadmium, lanthanum, aluminum and lead) glasses. Reduction of crystallite formation in reduced gravity will provide a more reliable methodology to determining phase transformations involved in the devitrification processes for these materials.

It is the intent of this study to utilize microgravity processing of HMGL materials to improve our understanding of the microstructure and processing characteristics for HMFG type glasses. Prior work with fiber annealing experiments of commercially provided ZBLAN fiber indicated that nucleation phenomena are reduced in reduced gravity. These observation provide an incentive to perform further comparisons between ground based experiments in various HMFG formulations. Laser scattering experiments of fluorozirconate glasses heated above the crystallization temperature will provide size and distribution information of precipitated phases in the glass. The data is to be analyzed in terms of the Avrami and Arrhenius equation to compare with ground based research in the literature. A three year proposed effort will lead to a space experiment hopefully being able to use the Laser Scattering Apparatus already in NASA's inventory. If that facility does not work very well for this experiment, the conceptual development of a glove box experiment will certainly evolve in this time period.

2.1 Prior Work

The structure of glass systems has been studied extensively over the last fifty years, developing a fairly good foundation for its properties. Unfortunately most of that knowledge base has been devoted to systems based on silica, which behave in a generally consistent framework.[1] However, glasses prepared from systems other than silica, can also possess useful characteristics for applications as optical devices. . The limiting factors imposed on the usage of these materials is normally due to instabilities which have not been resolved in producing these materials routinely. For instance, the heavy metal fluoride glasses (HMFG) or fluorozirconates possess unique infra-red transmission properties, but producing a formulation that behaves consistently still presents a problem even after over 20 years of research and development. HMFG and other unstable glass systems present an entirely different perspective on the structure and behavior of glass. Although a tremendous amount of research activity was pushed forward in the 1980's to develop the highest infra-red transmitting optical fiber available on the world market, we still do not have a good understanding of the HMGL structure and how this structure

provides the observed characteristics of the various materials currently used for optical fiber applications.[1-3].

The study of heavy metal fluoride glasses as a class, provides a unique system in that its properties as an infra-red optical fiber has great commercial appeal; yet, the fundamental science required to bring the material concept into a large volume market is still lacking. Prior to this most recent work on the effects of gravity on the crystallization of ZBLAN, there appears to have been two distinct periods in the materials science studies on HMGL materials. The original pioneering work by Poulain in the early 1970's provided original developments into the properties of ZF_4 as a glass former and the interesting infrared transmission properties for systems based on this chemical framework. Other fluorides making up these systems include LaF_4 , BaF_2 , AlF_3 , and NaF . The acronym for this class of materials is called ZBLAN.

A tremendous wave of activity surged forward in the early 1980's when the Department of Defense and some commercial interests realized the potential for the low attenuation observed in high quality HMGL fibers. Unfortunately the best stability was attained primarily by trial and error with systems composed of various combinations of the above fluorides. Dr. Danh Tran formed a commercial enterprise, Infrared Fiber Systems (IFS), and developed one of the most stable formulations using his own proprietary composition of ZBLAN. Other commercial entities have done the same. Unfortunately this system still tends to crystallize during fiber processing in a 1g environment. It is still not clear whether or not latent nucleation sites occur in the preform or develop in the fiber drawing process.

Much of the early work with determining the processing parameters associated with HMFG, has been concerned with DSC and DTA analysis of the various vitreous and non-vitreous phases formed during heating to the liquidus temperature. In addition some optical and microscopy work has been oriented toward identifying crystal formation and quantifying growth rates. These research activities provided some insight into which crystallites were preferentially formed during the devitrification process; but very little progress was made in determining the mechanisms for the processes.[4-8] A number of compositions were tried with many experiments directed at finding a composition with a wide working range between the glass transition temperature T_g and the crystallization temperature T_x . The overall glass properties were optimized for $\Delta T = T_x - T_g$ since fiber drawing operations prefer a wider working region. ZBLAN was determined to be the optimal mixture for fiber drawing.

Most of the above research has analyzed the isothermal growth kinetics in terms of the Avrami equation:

$$X = 1 - \exp(-kt^n) \quad (1)$$

where X is the fraction crystallized isothermally in time t and k is the crystallization growth constant which depends on the rate of crystal growth and the number of nuclei

that are forming crystals. The factor n is the Avrami exponent and depends on the morphology of the crystal growth. For the fluorozirconate materials a value of 3 has been routinely used for n . The crystallization activation energy has been estimated fairly well using the Arrhenius equation:

$$k = v \exp(-E/RT) \quad (2)$$

where E is the energy of activation for crystallization.

The best summary of the DSC results are given in Table I.

Table I. Kinetic values from prior work.[8]

Glass	n	$v(s^{-1})$	E (kJ/mole)
ZrF ₄ -BaF ₂	3.2 ± 0.3	3.5×10^{28}	371
ZrF ₄ -BaF ₂ -LaF ₃	3.2 ± 0.2	7×10^{21}	332
ZBLAN	-	-	-

Optical microscopy of particulates nucleating and growing in HMFG experiments which were performed at temperatures above the glass transition temperature were also used in attempting to determine kinetics and growth mechanisms.[9-12] In most cases these experiments were performed in parallel with DSC/DTA experiments with composition as a variable.

A smaller number of researchers have used light scattering experiments to quantify nucleation and growth, as it affected the ability of the glass to transmit light. Although the concept of using the light scattering parameters to monitor the nucleation and growth of crystallites in the optical glass was generated in this early work, the usage of the methodology was very limited.[13-20] Light scattering was chosen as a method to differentiate between intrinsic and extrinsic losses. For instance, taking the total light loss as:

$$\text{Total Loss} = \text{Absorption Loss} + \text{Scattering Loss} \quad (3)$$

Then,

$$\text{Scattering} = B/\lambda^4 + C/\lambda^2 + D$$

where B and C represent the contributions from Rayleigh and Mie scattering respectively. Raleigh scattering occurs from index of refraction fluctuations in the fiber, whereas Mie scattering arises from particle and crystals developing in the glass. X-ray diffraction techniques were normally used to identify the nucleating particles, which were normally conglomerates of BaZrF and occasionally La. The following table was generated from this activity:[19]

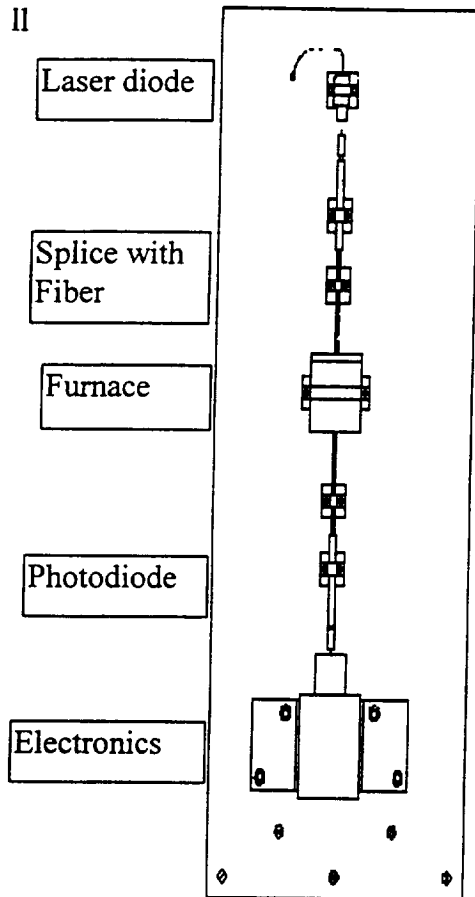
Particle	Size(μm)	Scattering
ZrF ₄	1-5	Mie
β -BaZrF ₆	50-100	Wavelength Independent
LaF ₃	>3	Wavelength Independent
ZrO ₂	10	Wavelength Independent
Bubbles	0.3 - 50	Wavelength Independent
Pt	0.1 - 0.5	Wavelength Independent

Results of these approaches allowed the researchers to identify contaminating particles, such as Pt and other particles which occurred, allowing methods to be developed to remove them from the process, thus improving the optical transmission characteristics of the material. Since no mechanism for growth was identified, the undesirable nucleation and growth of the Zr, Ba and La fluorides was not successfully handled with these approaches, but ZBLAN did show up as the best of the lot for optical fiber applications.

2.2 Experimental Apparatus

Fiber annealing and drawing experiments in reduced gravity in aircraft and sounding rockets were initiated in commercial programs in Canada and the US.[21-24] Independent results showed indications of reduced nucleation in commercially provided ZBLAN fibers. In another approach to determine if reduced gravity does reduce nucleation in ZBLAN, a recent 'quick and dirty' experiment was developed for the DC-9, in which the attenuation of a ZBLAN fiber was measured in transition through the reduced gravity of the parabolic flight. Some fairly elaborate experiments identified earlier in prior work, seemed much too complicated for initial experimentation in parabolic flight. We still have the complication of extreme nucleation in the high g portion of the parabola, hence we approached the temperature profile by heating up to a temperature below T_g until just before the g-level drops toward 0.001 g.

The apparatus flown on the DC-9 at Lewis Reserch Center is shown in figure 1 on the next page.



A diode laser at 633 nanometers was focused into a 150 mm ZBLAN fiber which then passed through a furnace fixture. The portion of the fiber in the furnace was maintained in a vertical orientation to minimize any motion during g level changes. Baseline data with no heat or no fiber are shown in figures 2-3. During the parabolic flights, a preheat to just below the glass transition region was maintained throughout the high g, and then rapid heating to various temperatures above T_g was performed as the g level decreased. Result is shown in figures 2 - 27. After the DC-9 flights, ground based experiments, duplicating the temperatures attained during flight were performed. These results are shown in figures 28 -33.

Figure 1. Schematic of apparatus used to observe changes in light transmission with gravity.

2.3 Results

The flight data consistently shows a rapid drop in intensity, which is independent of g level changes, indicating that a mechanical response to the rapid heating occurs during transition into low g. All sub-systems performed as designed. The major variability, which is common in this type of experiment, is trying to get the temperature of the fiber up to the desired temperature quickly from the pre-heat temperature.

Figure 2.

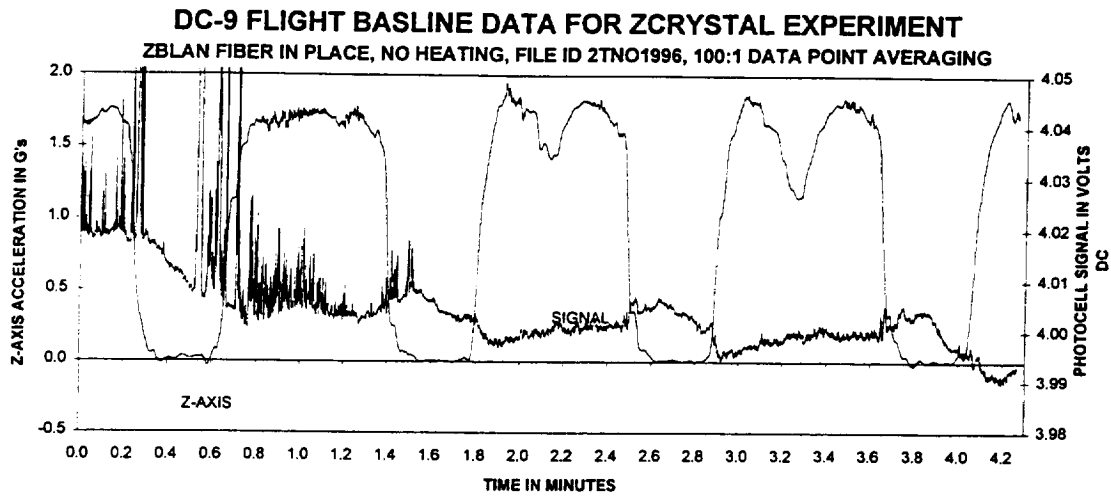


Figure 3.

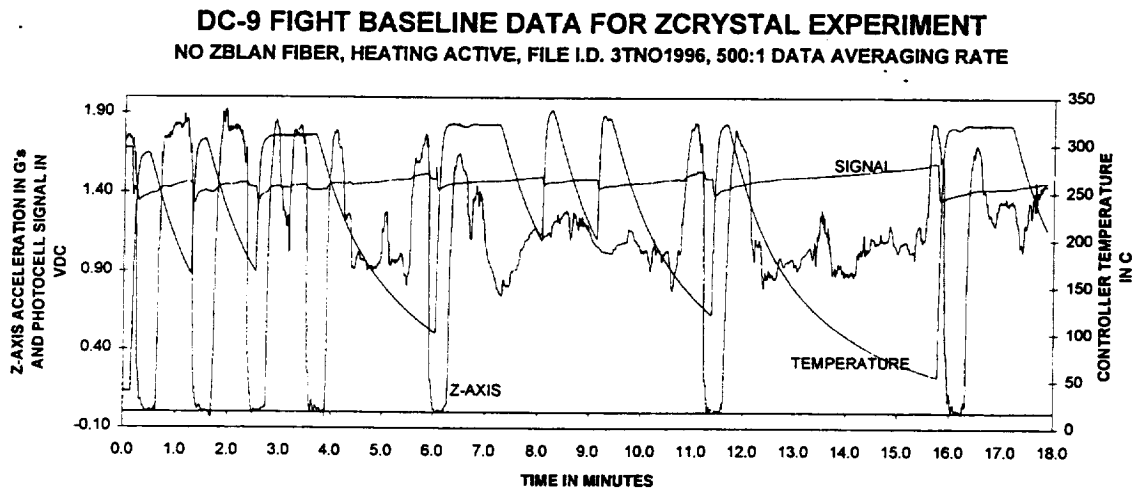


Figure 4.

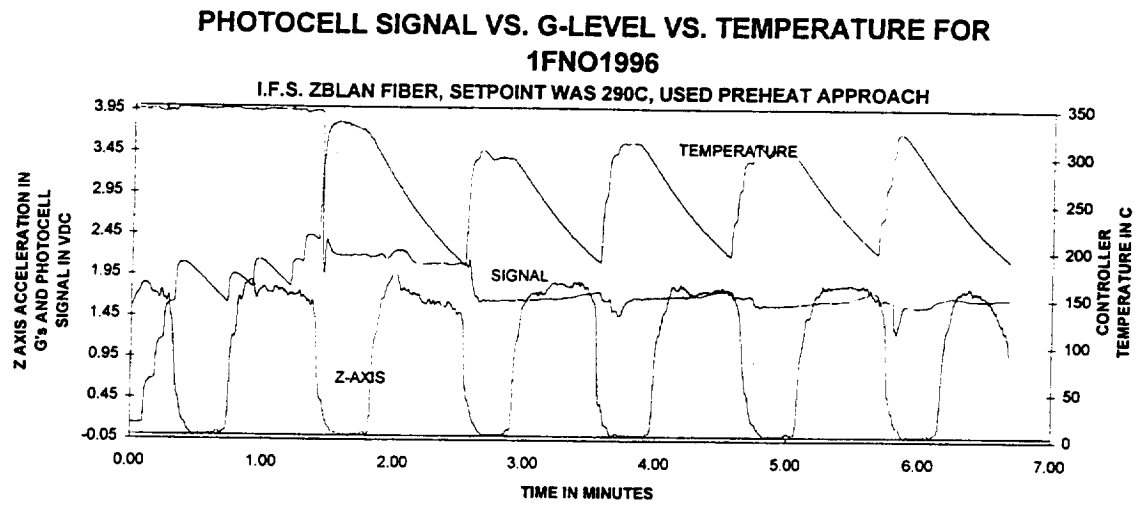


Figure 5.

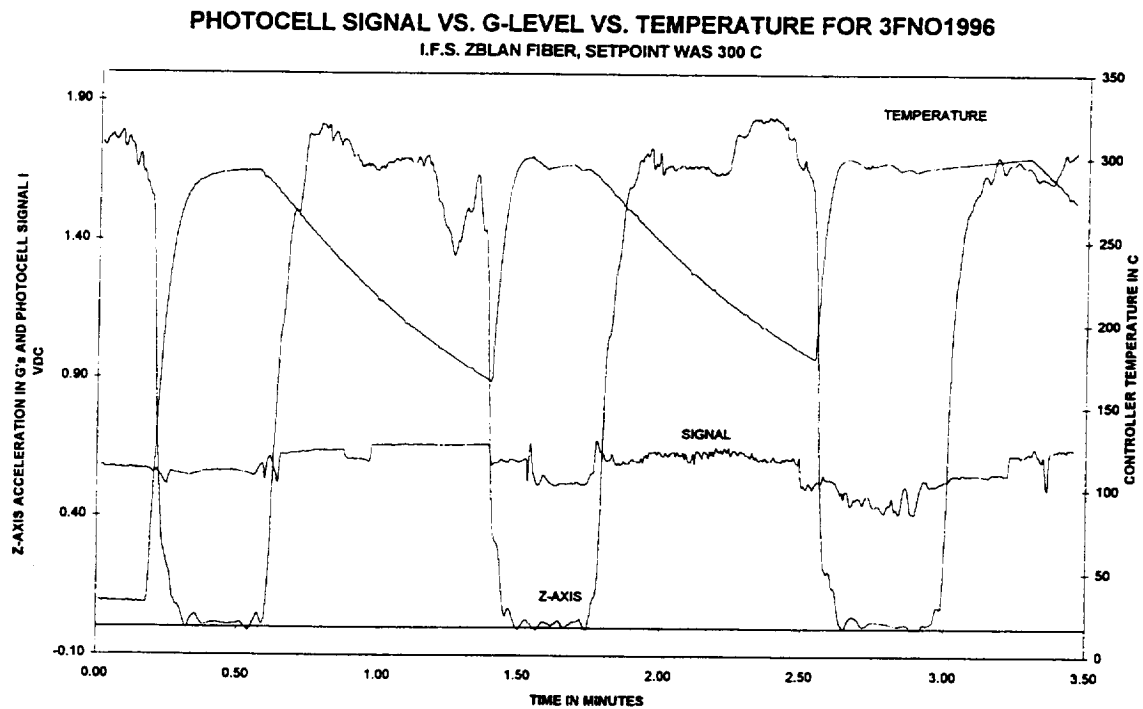


Figure 6.

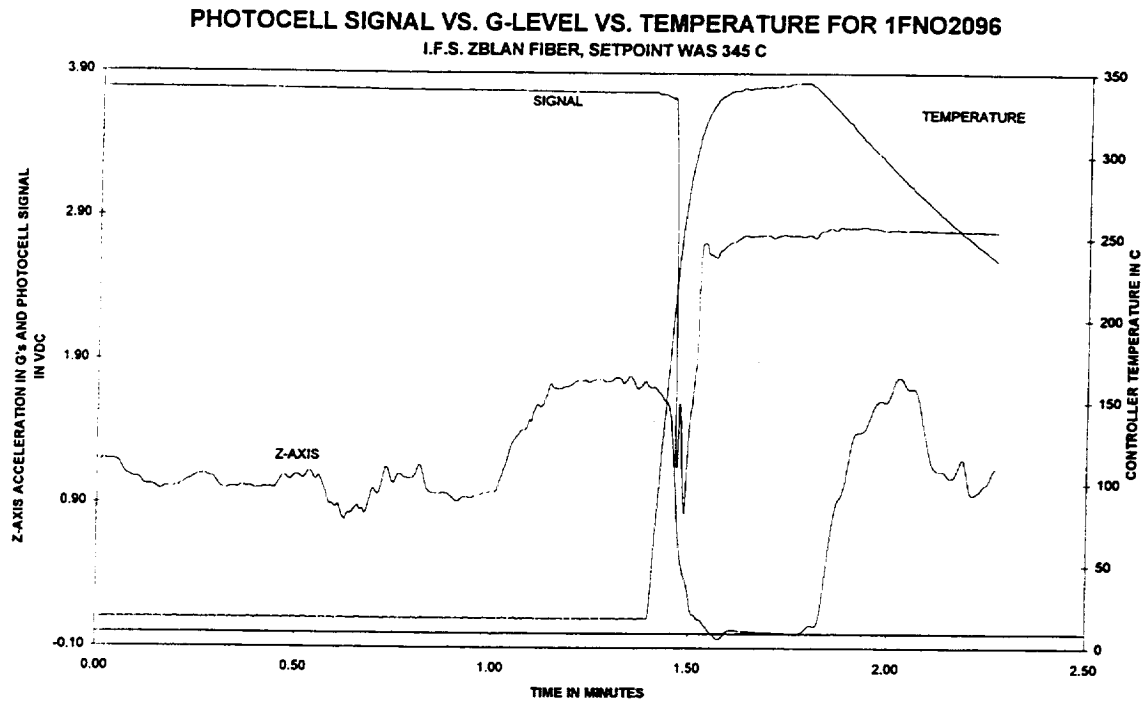


Figure 7.

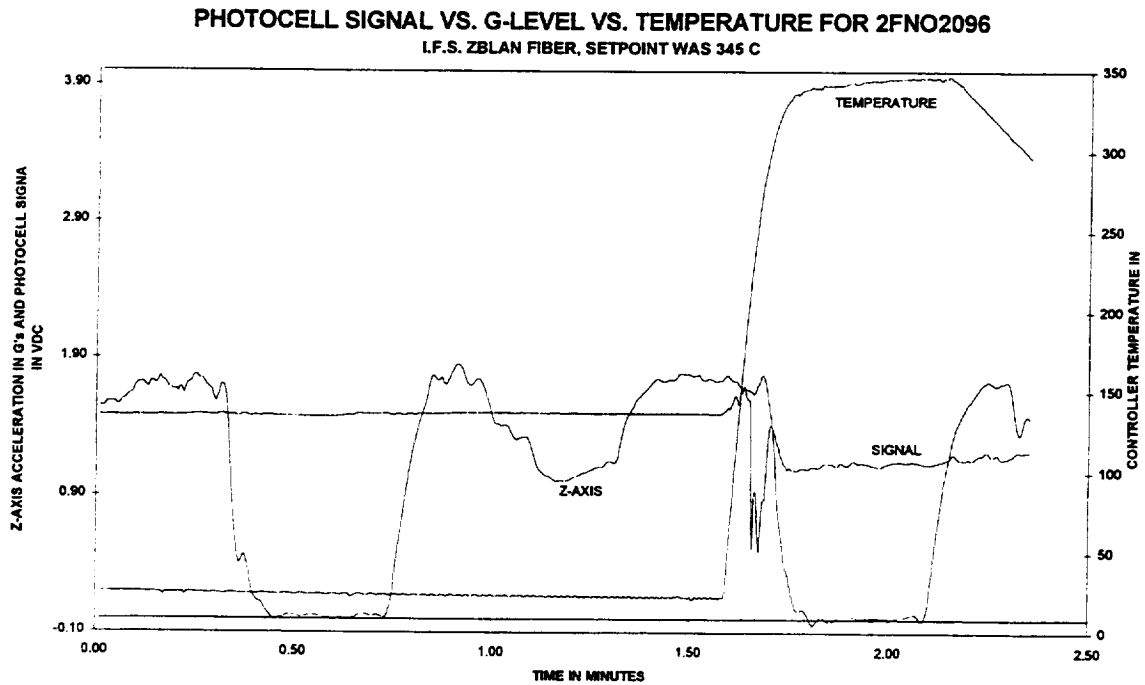


Figure 8.

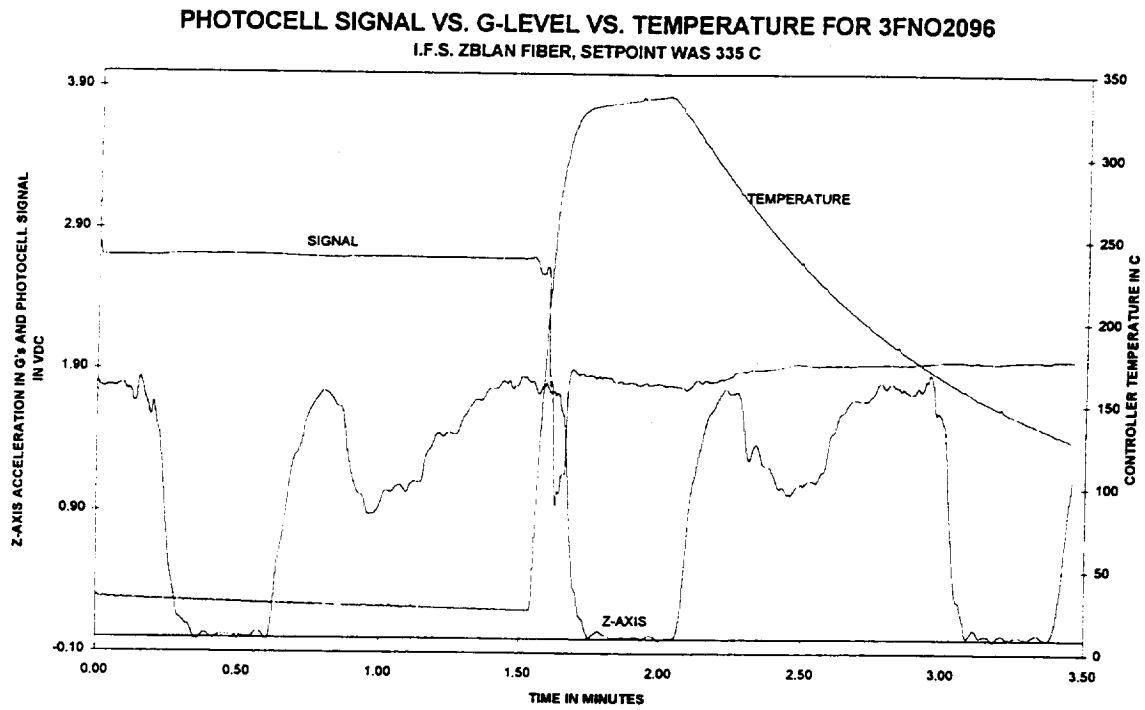


Figure 9.

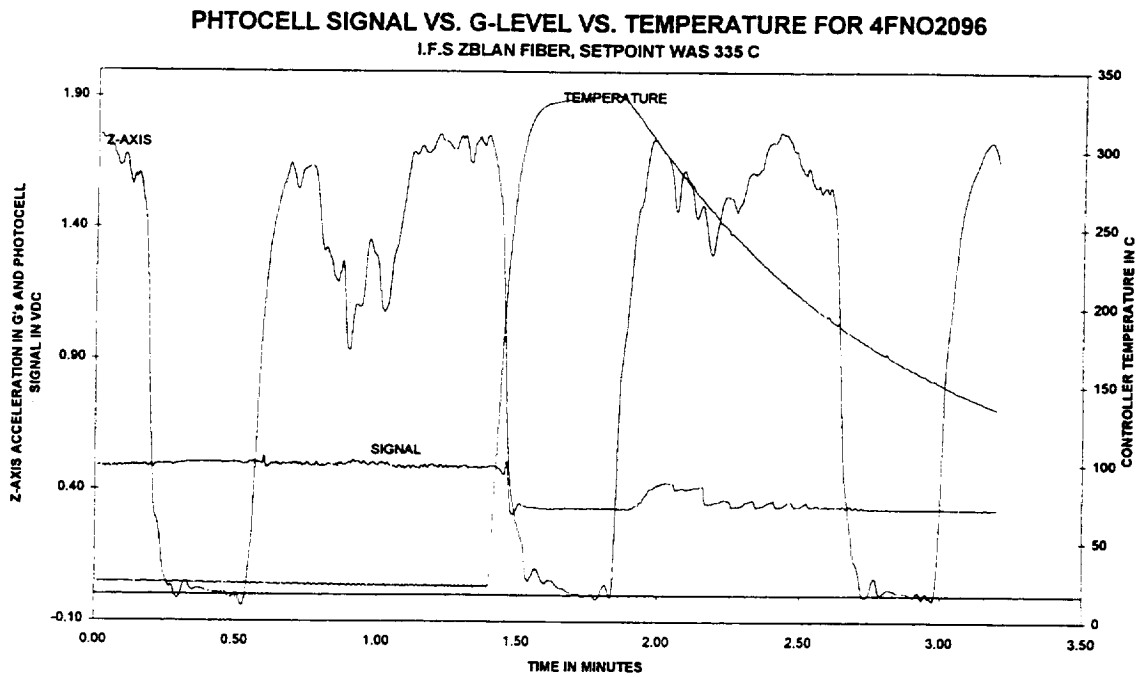


Figure 10.

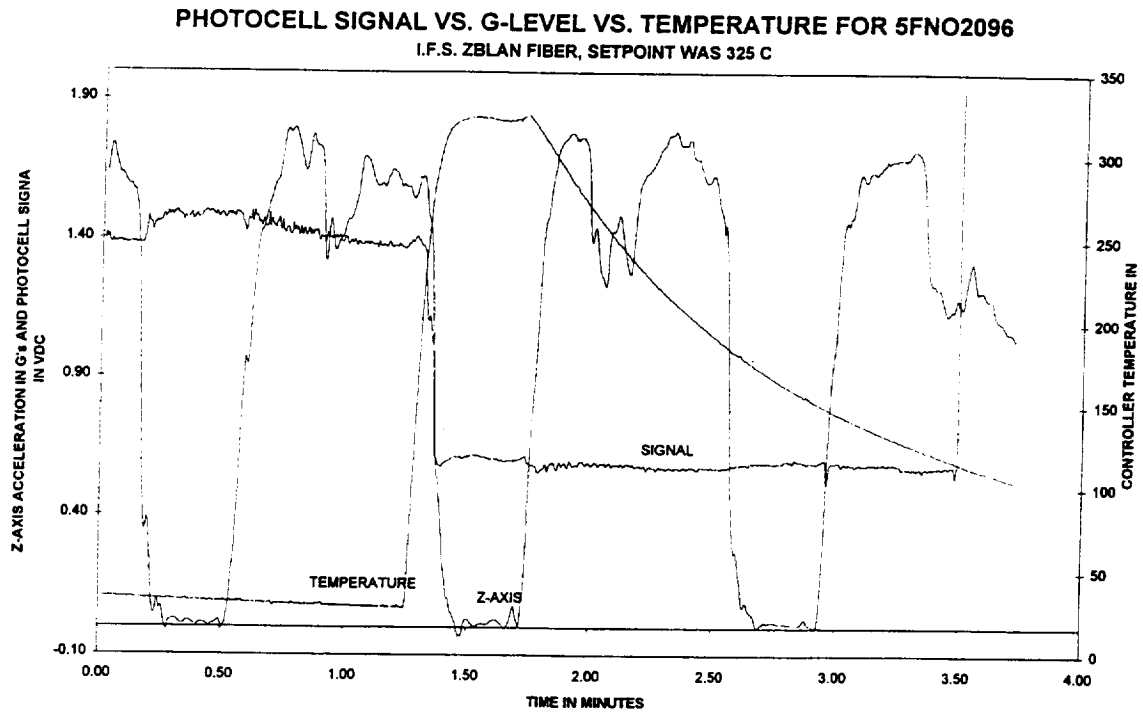


Figure 11.

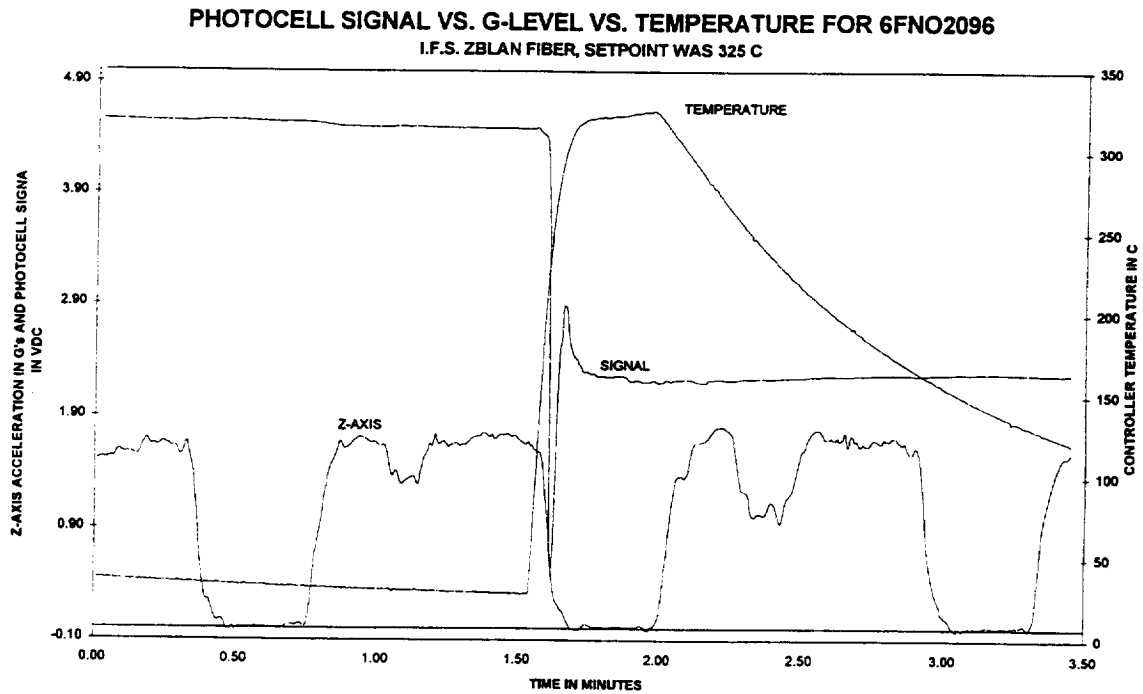


Figure 12.

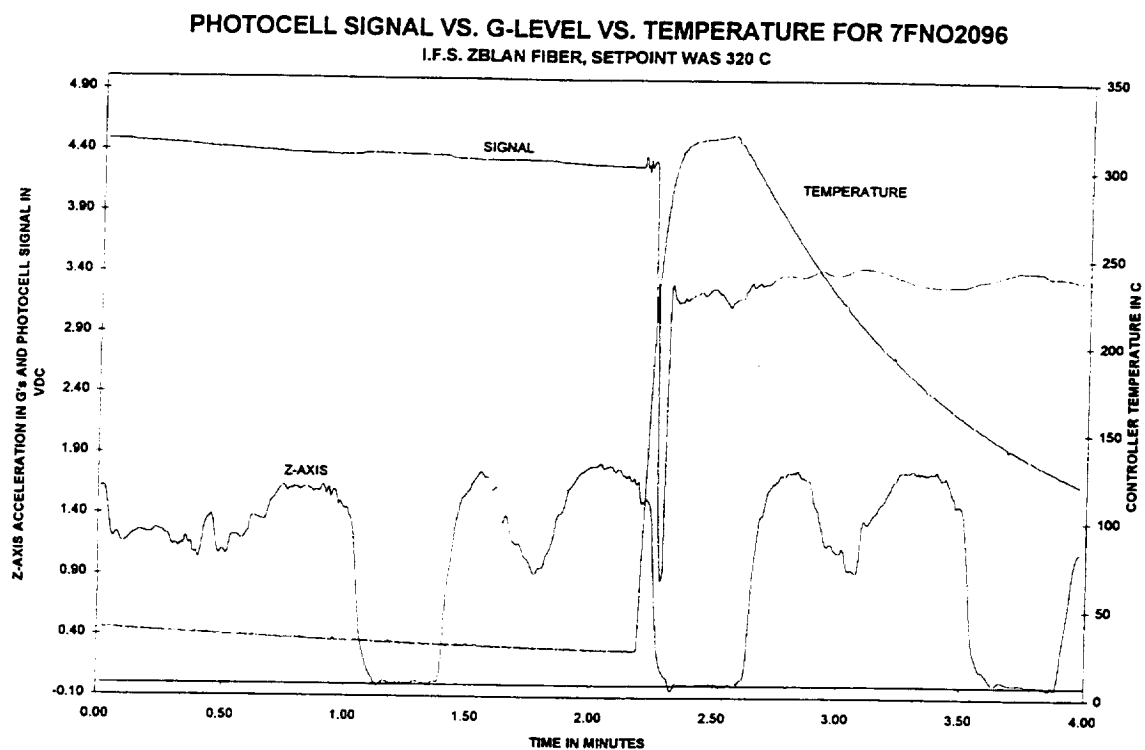


Figure 13.

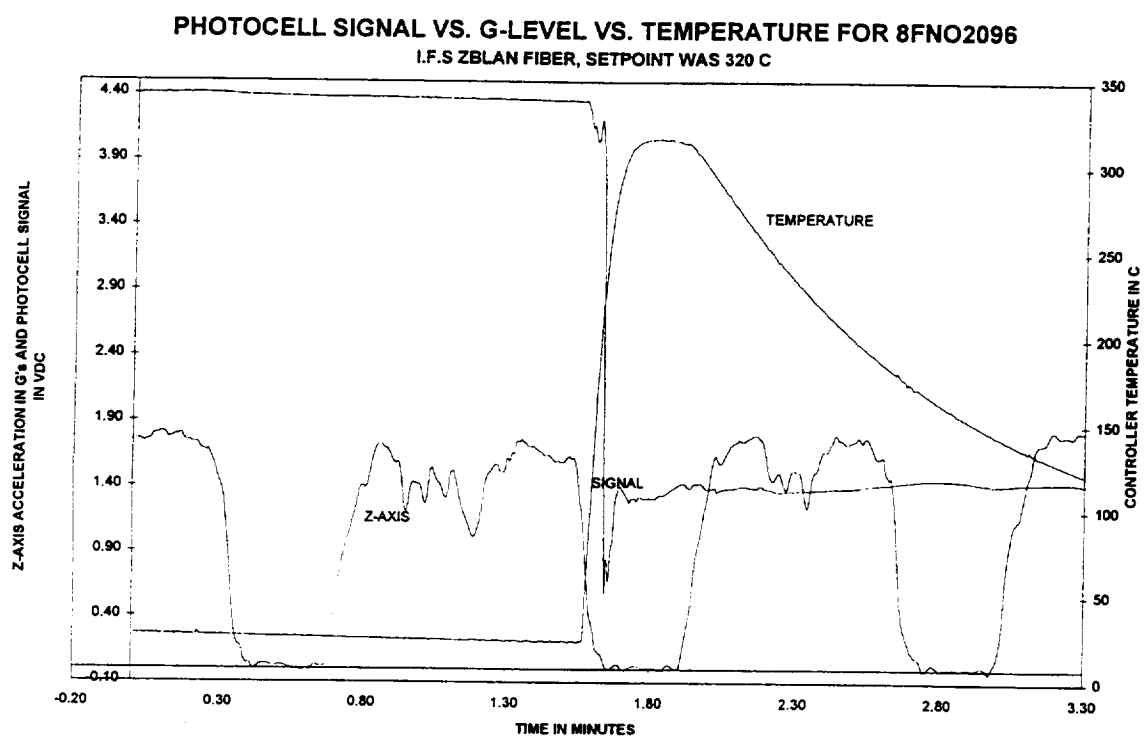


Figure 14.

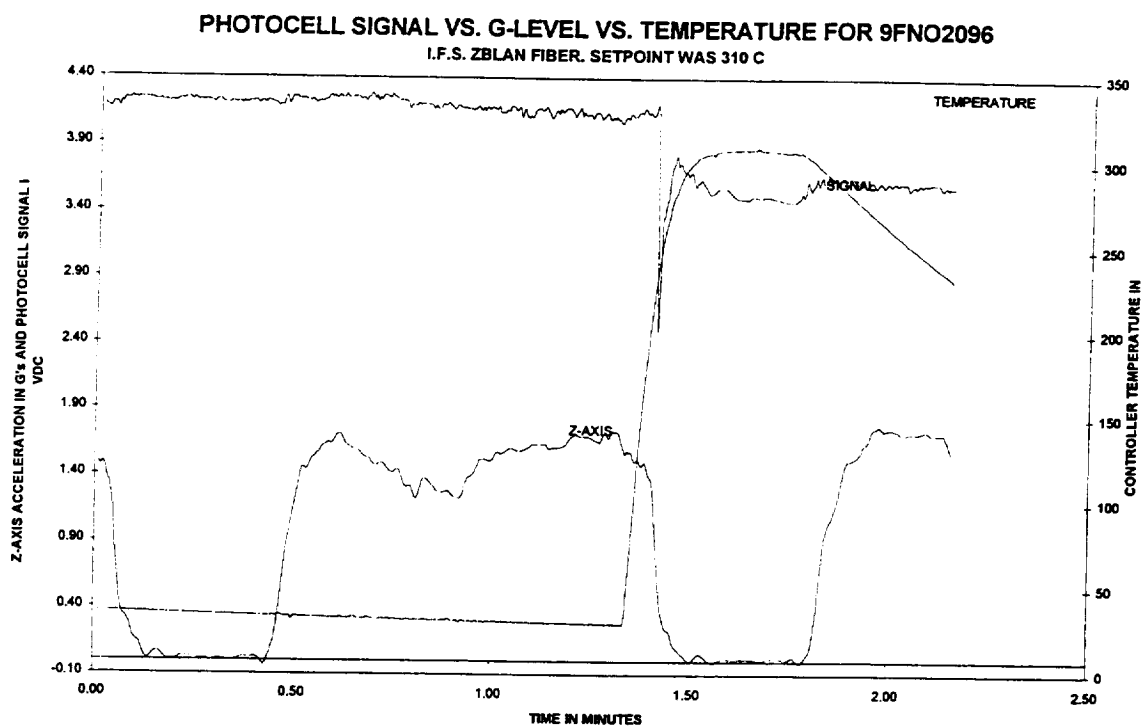


Figure 15.

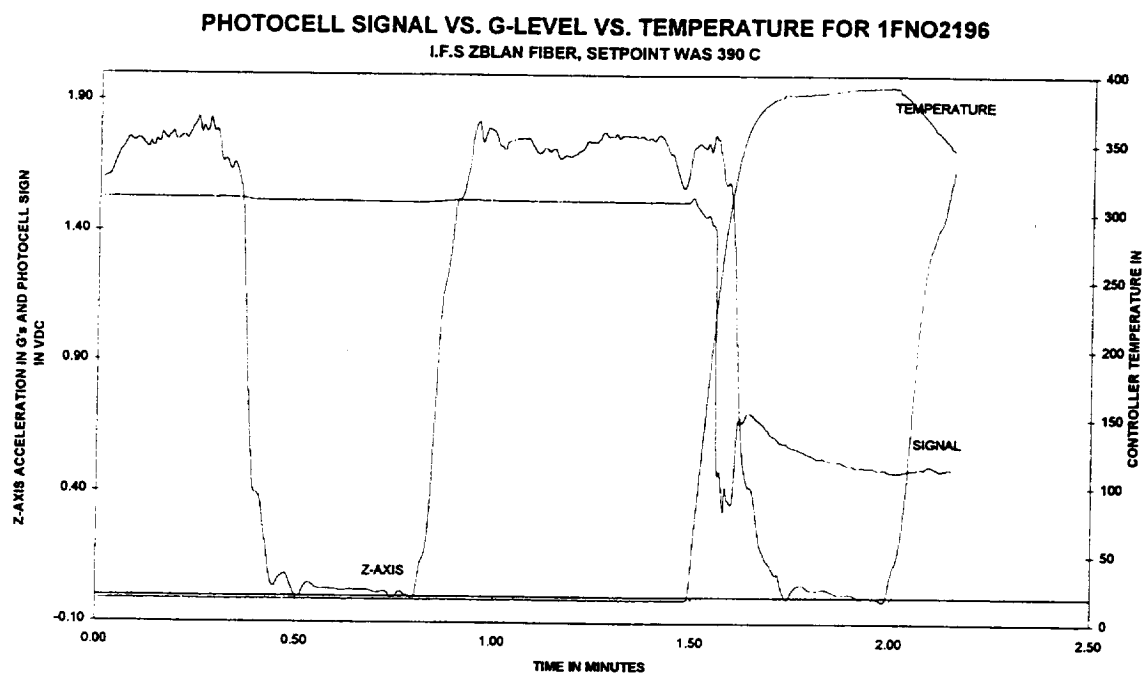


Figure 16.

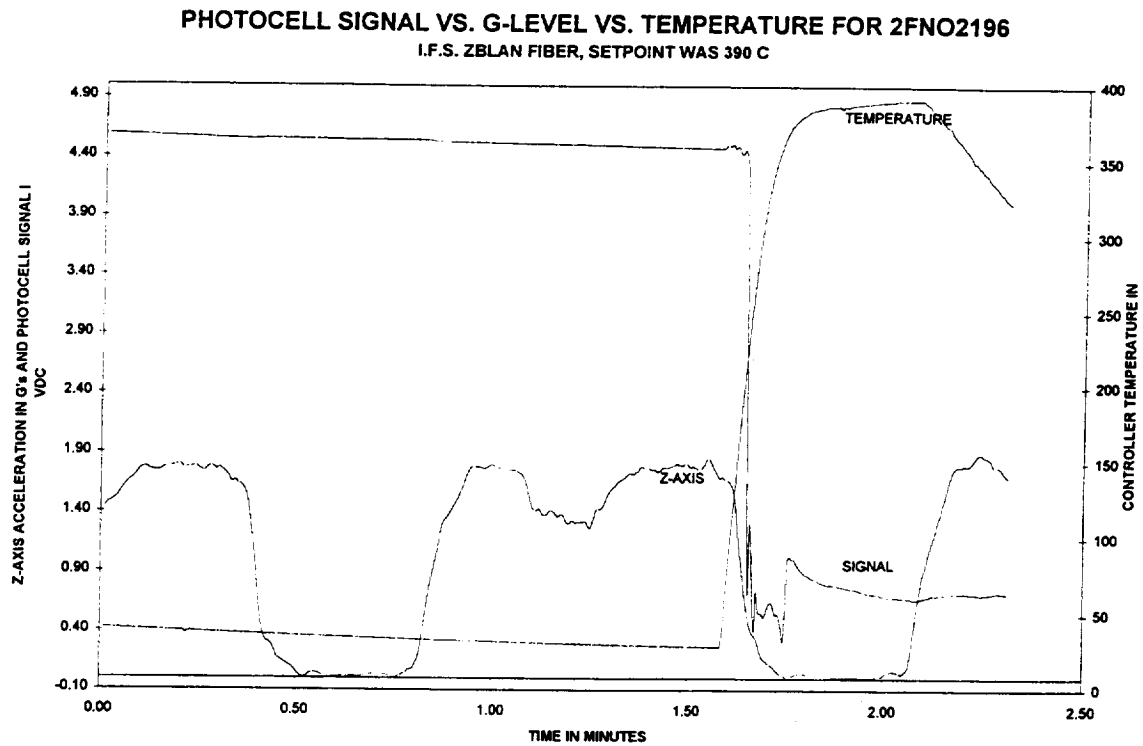


Figure 17.

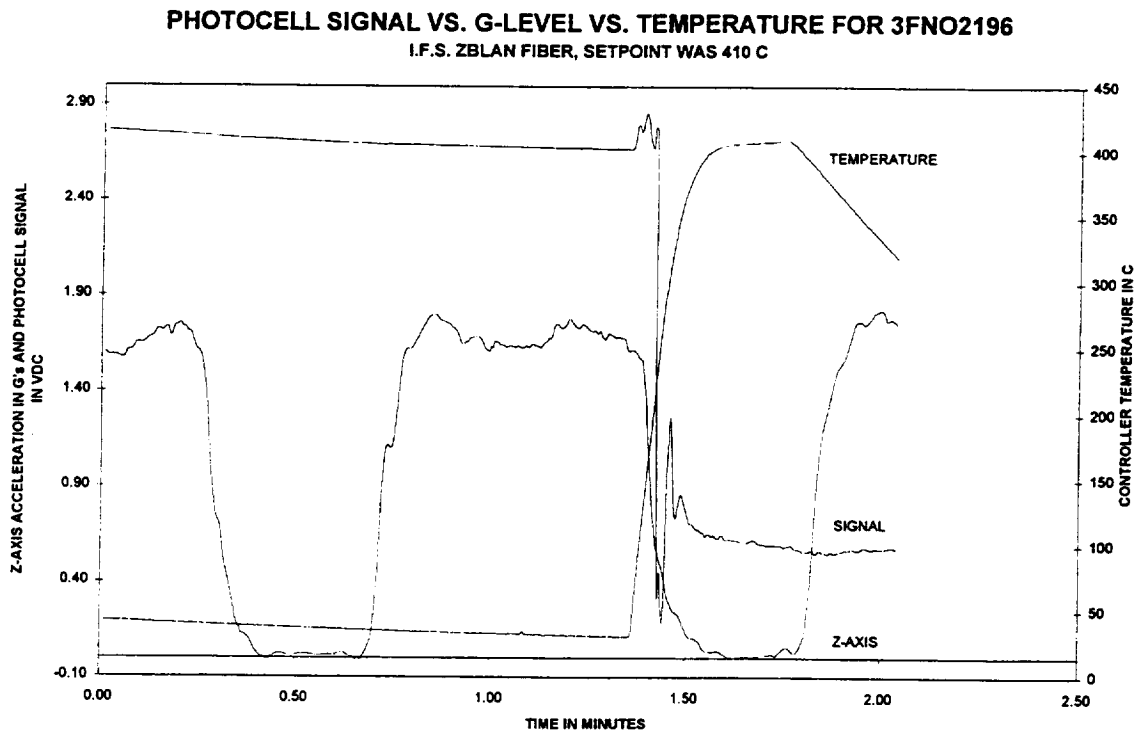


Figure 18.

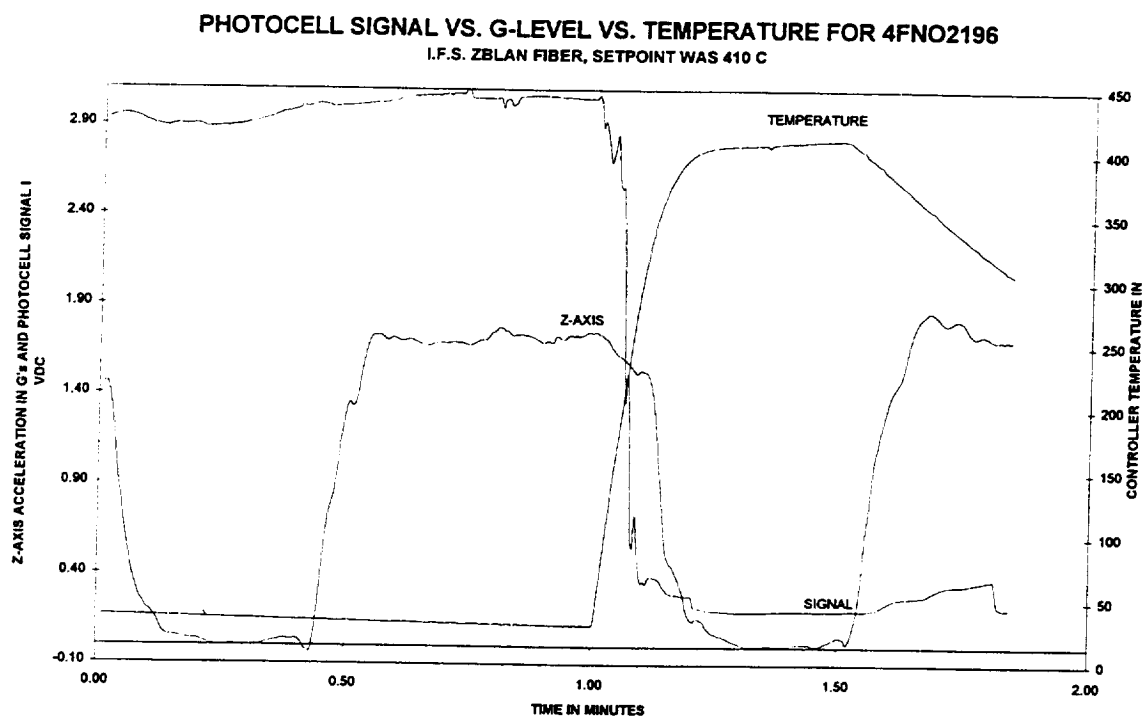


Figure 19.

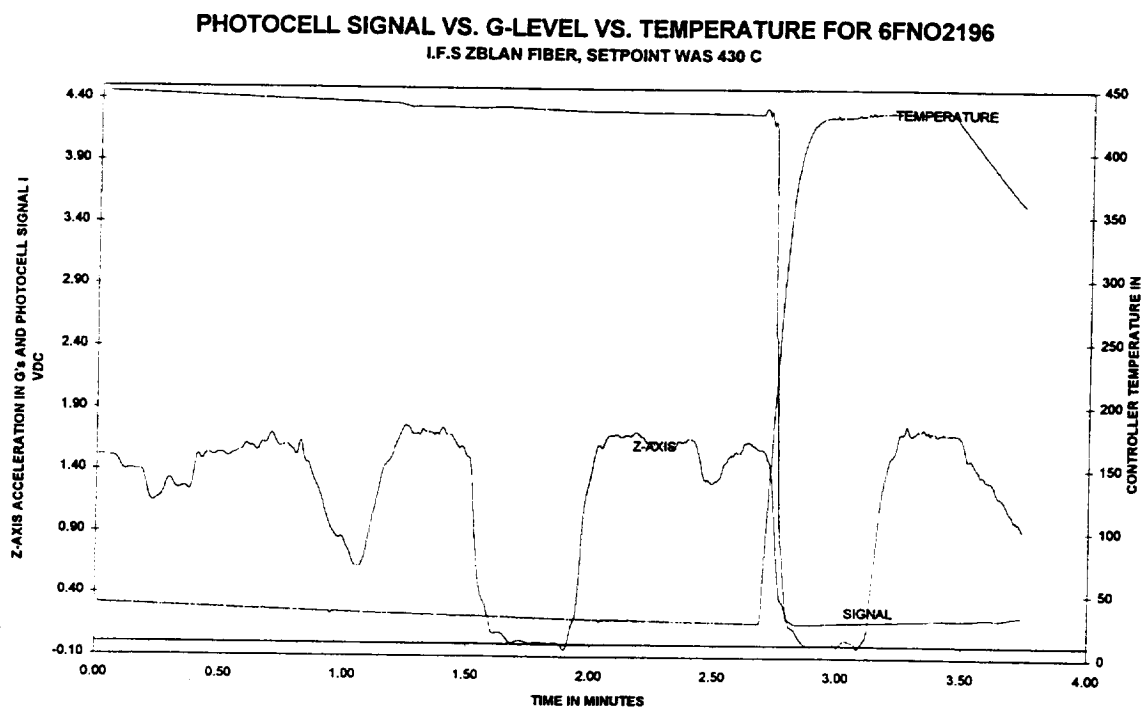


Figure 20.

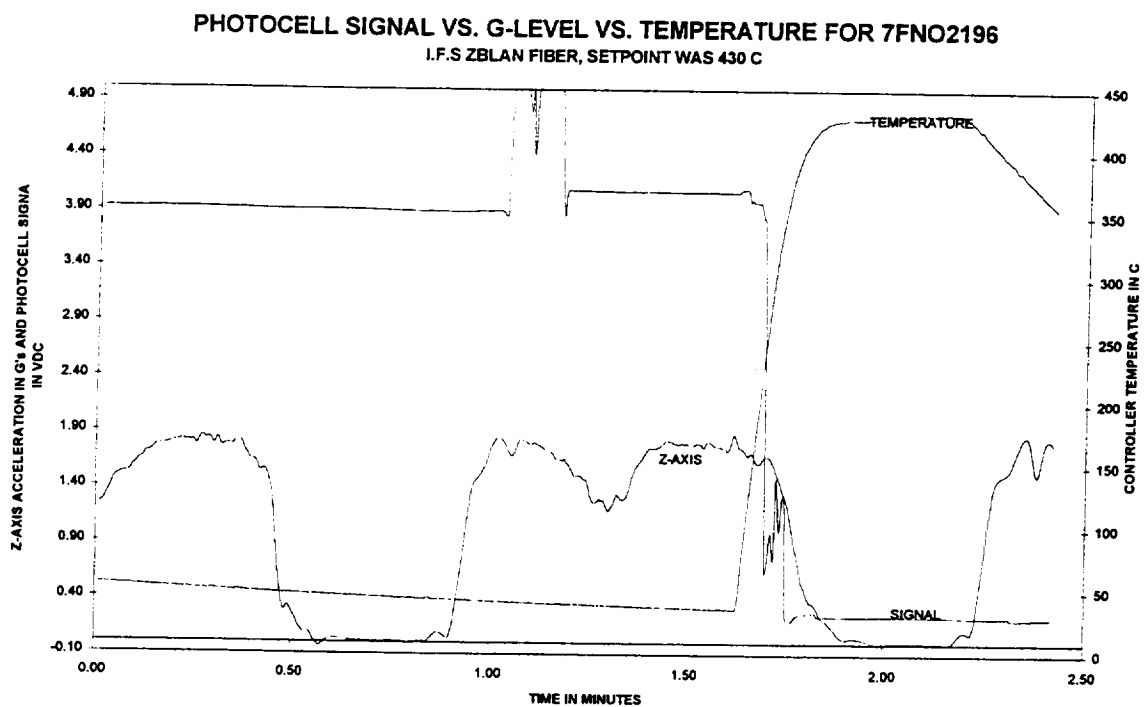


Figure 21.

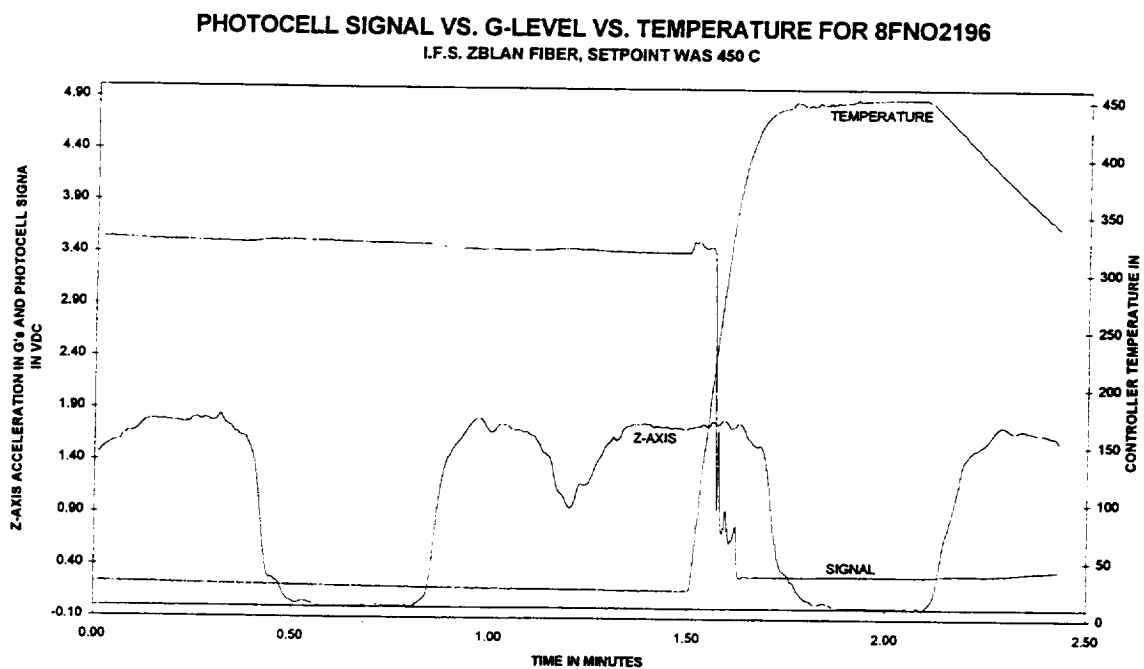


Figure 22.

PHOTOCELL SIGNAL VS. TEMPERATURE FOR GROUND RUN 1GNO1996
I.F.S. ZBLAN FIBER, SETPOINT WAS 290 C

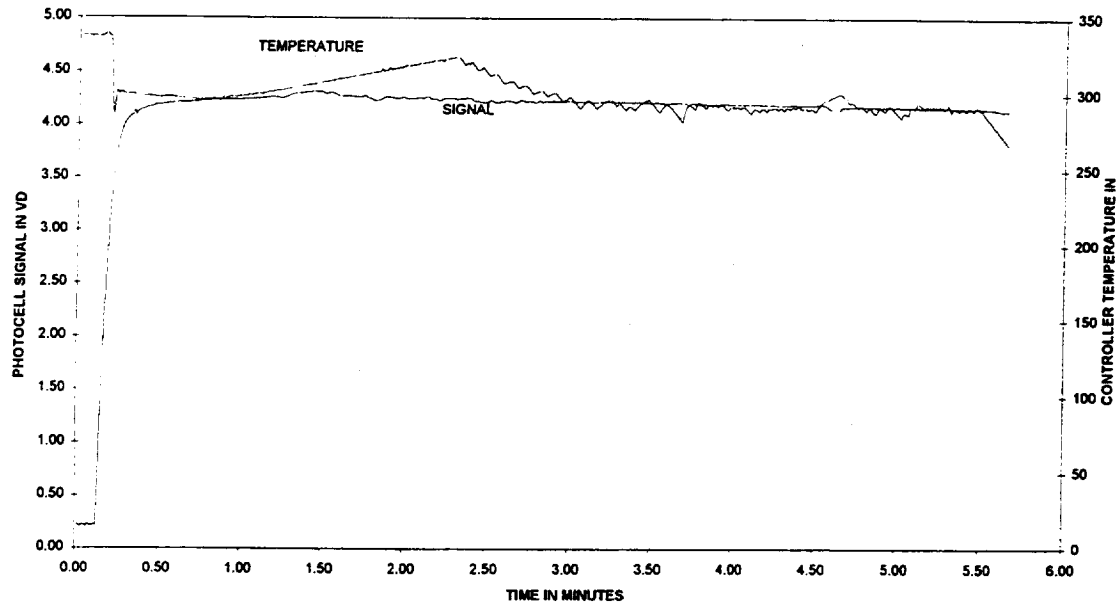


Figure 23.

PHOTOCELL SIGNAL VS. TEMPERATURE FOR GROUND RUN 2GNO1996
I.F.S. ZBLAN FIBER, SETPOINT WAS 300 C

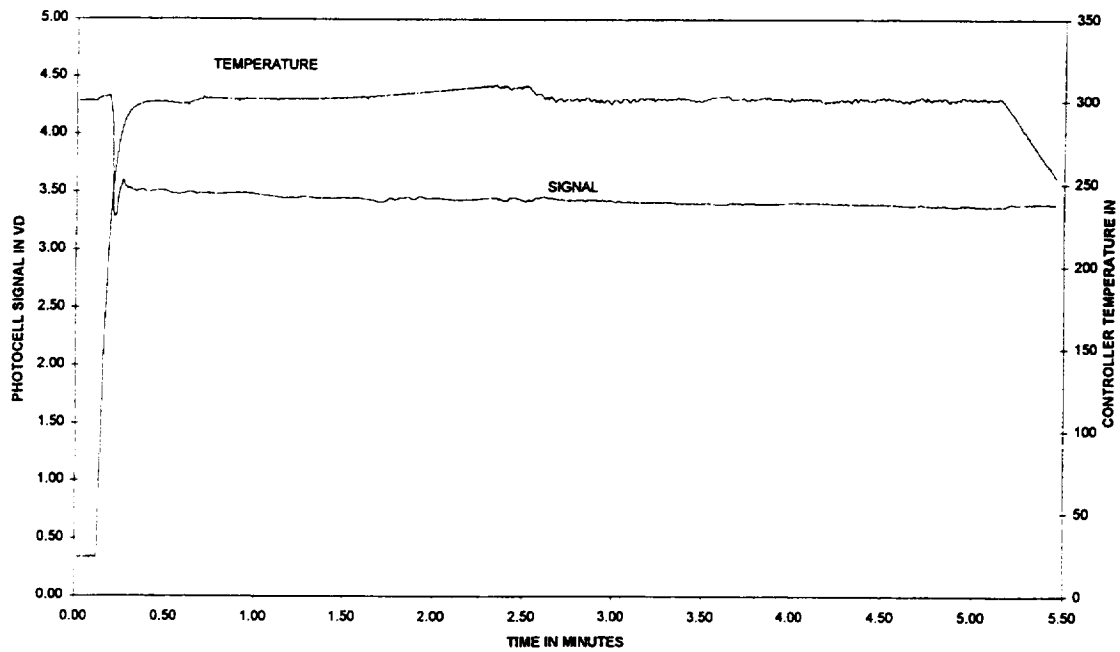


Figure 24.

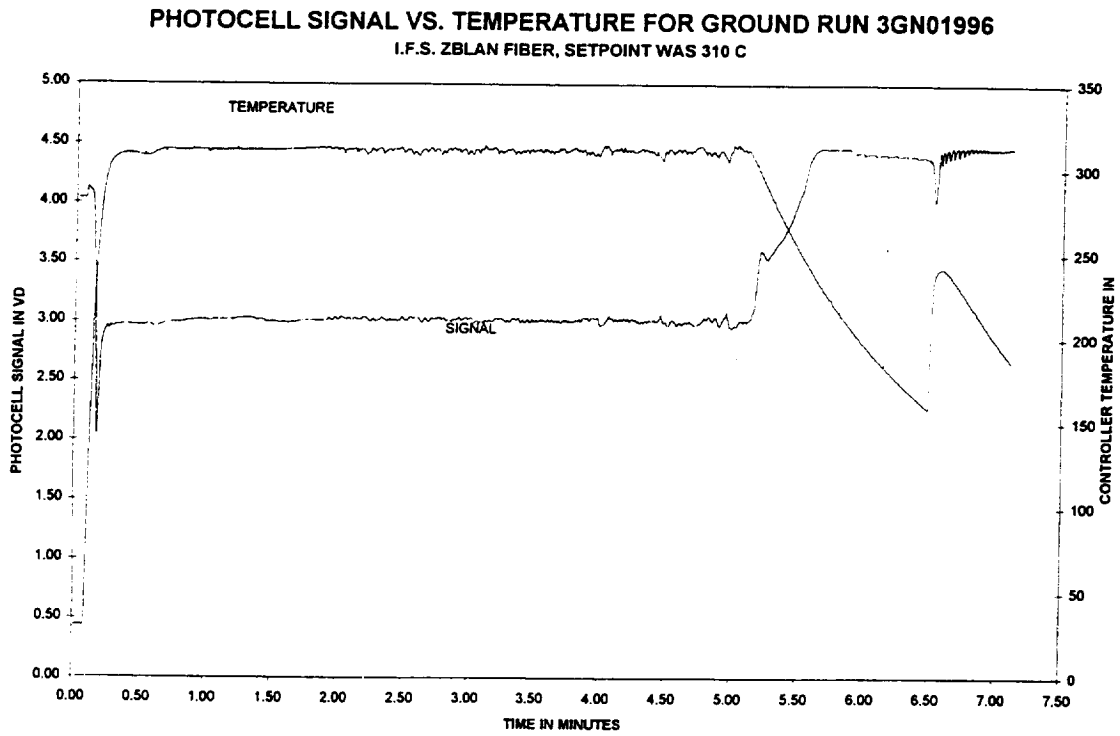


Figure 25.

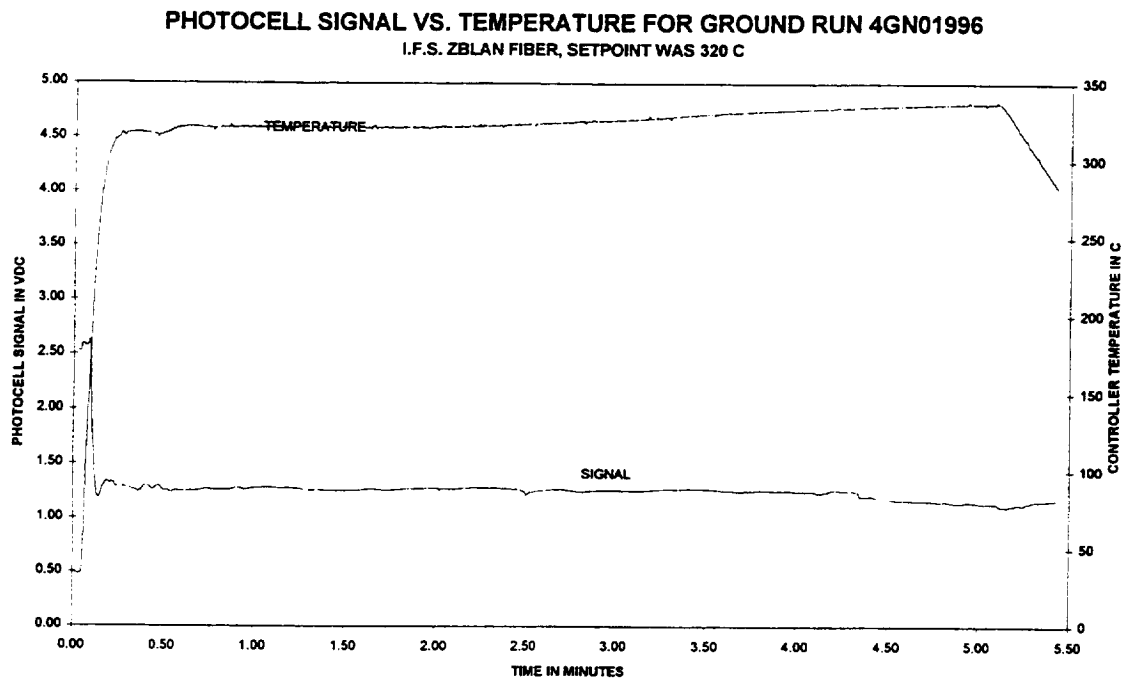


Figure 26.

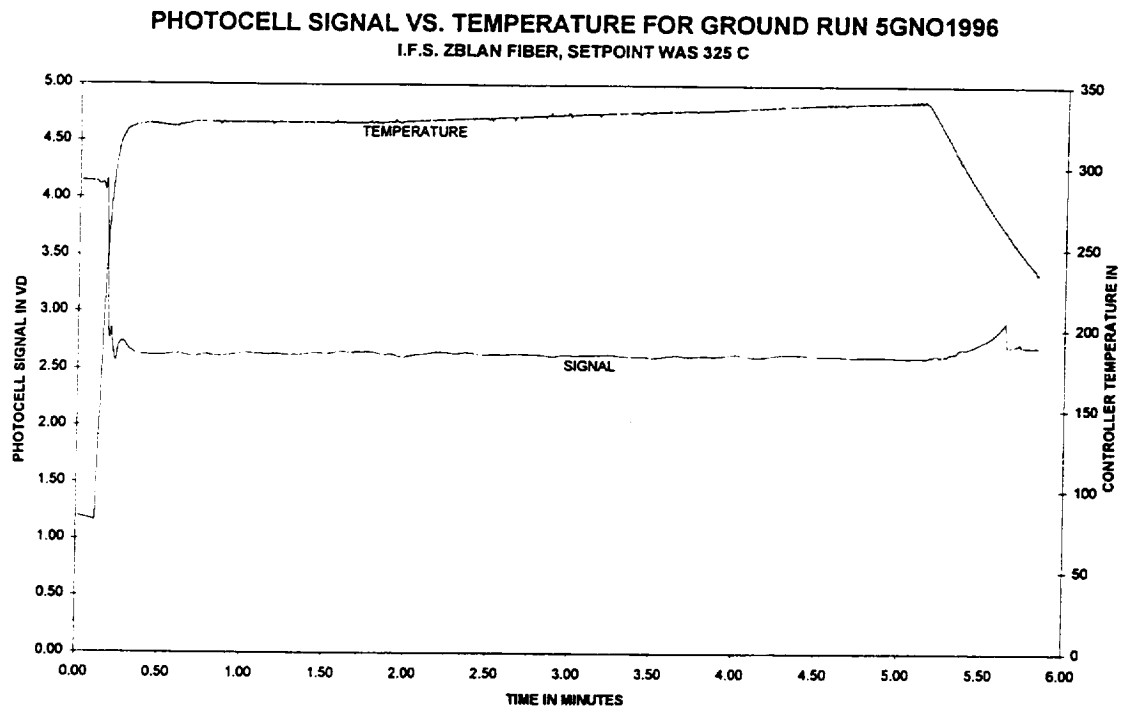


Figure 27.

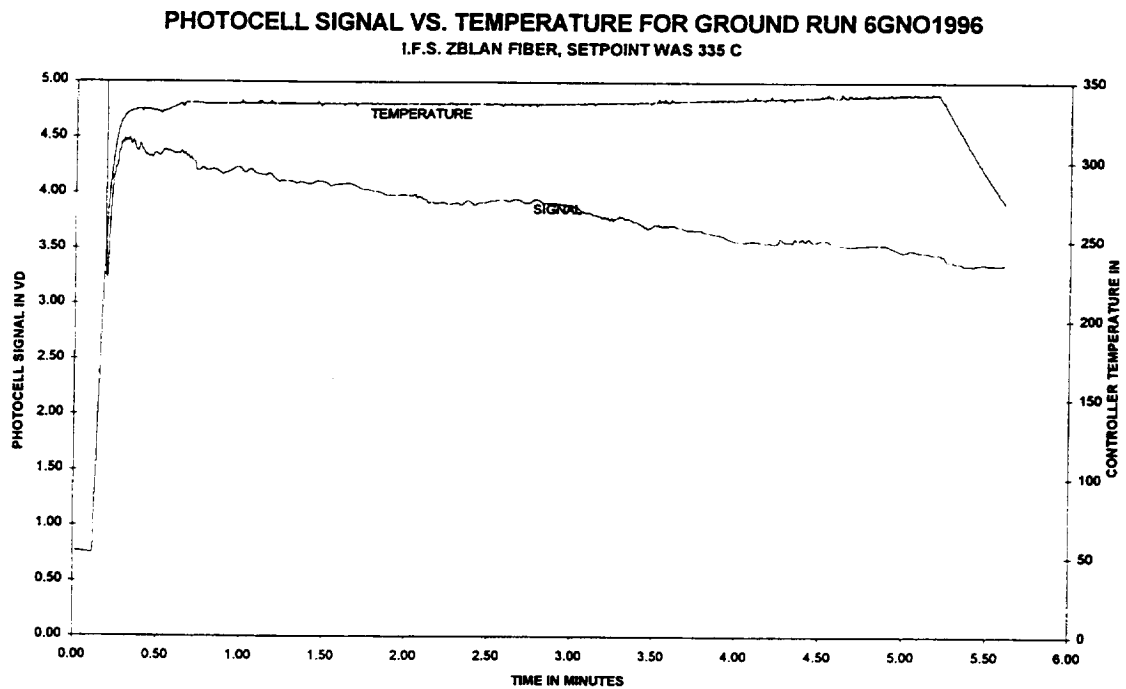


Figure 28

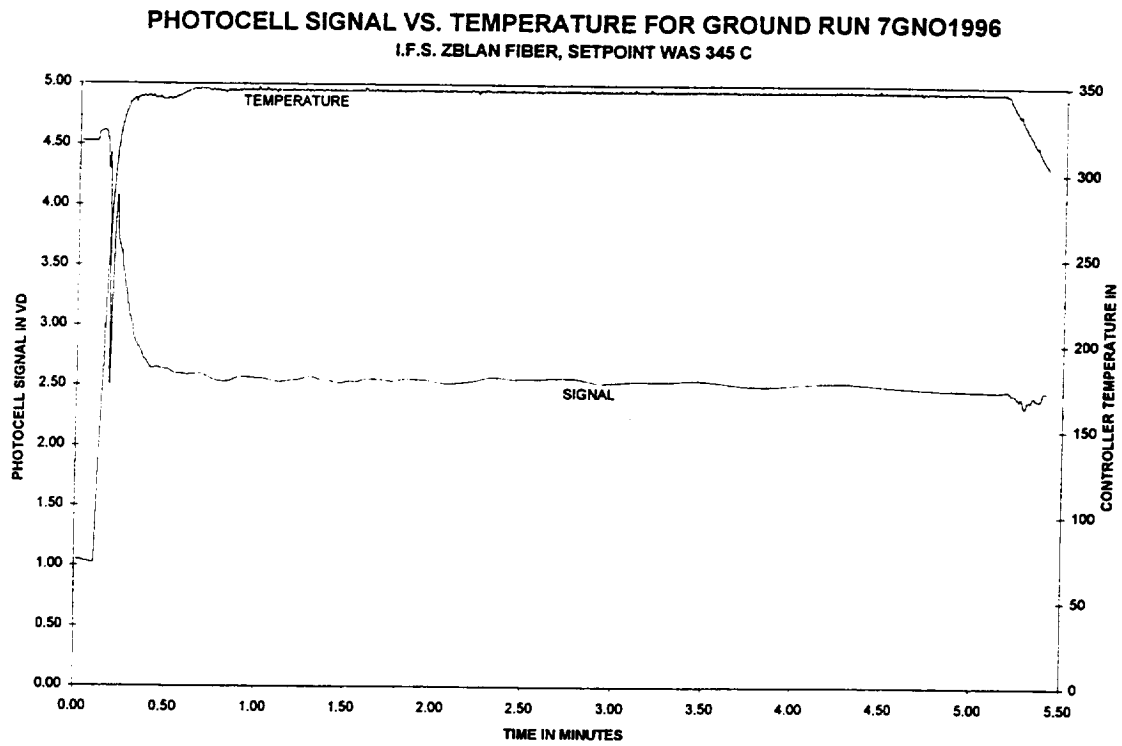


Figure 29.

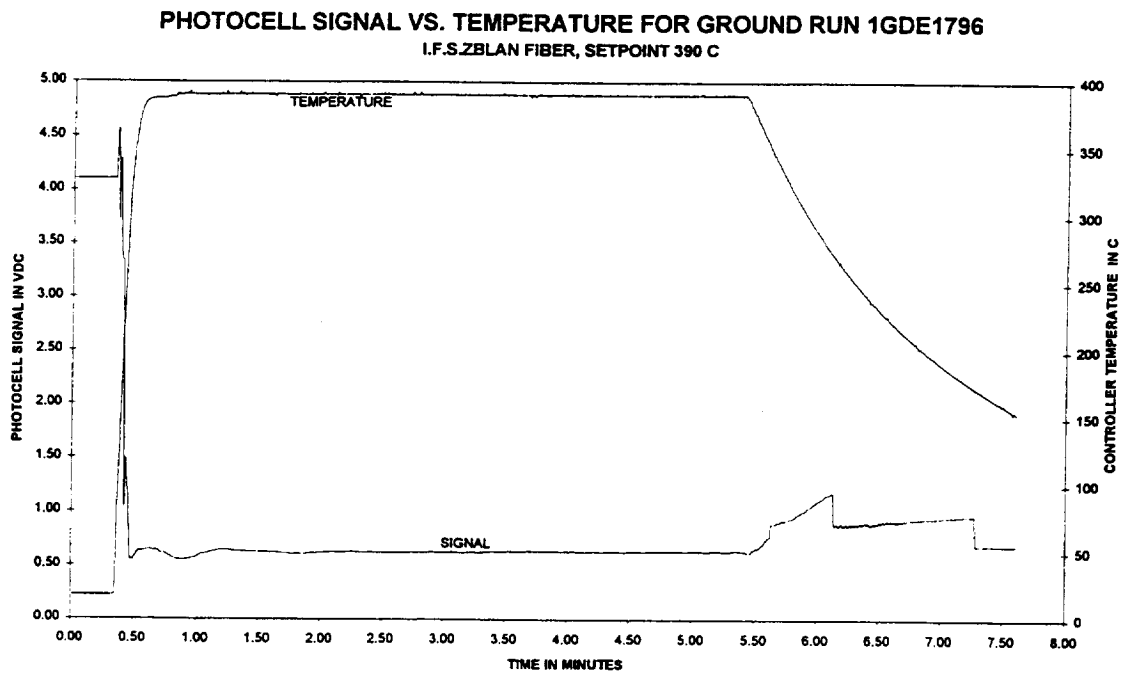


Figure 30.

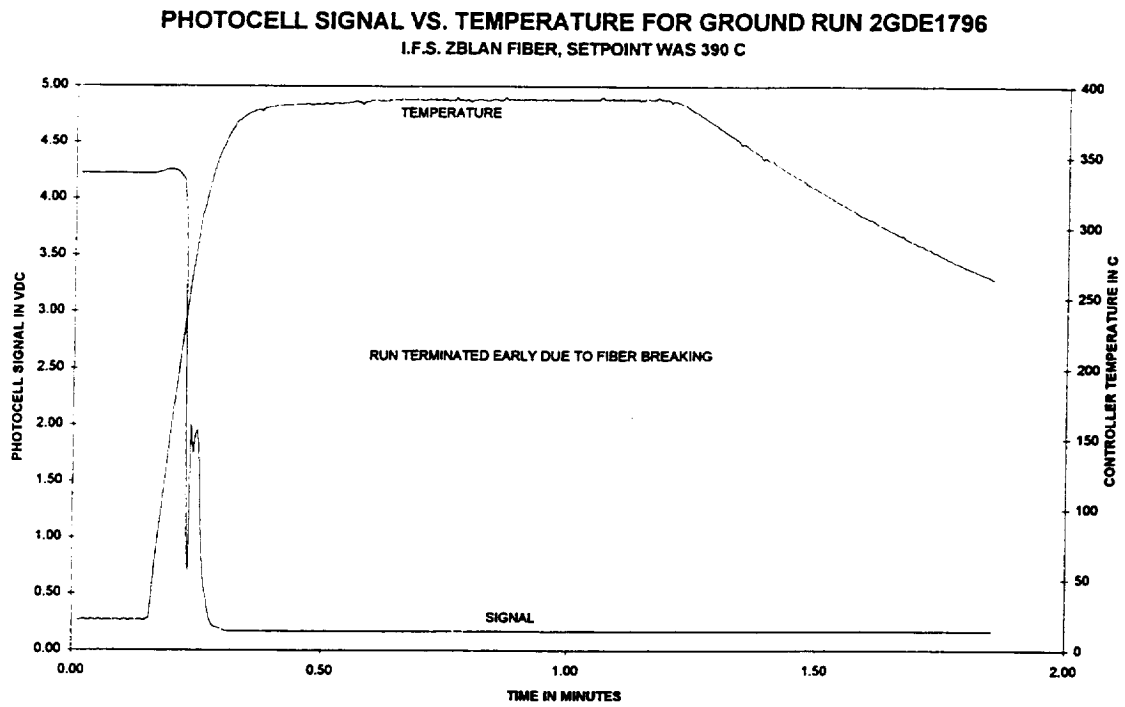


Figure 31.

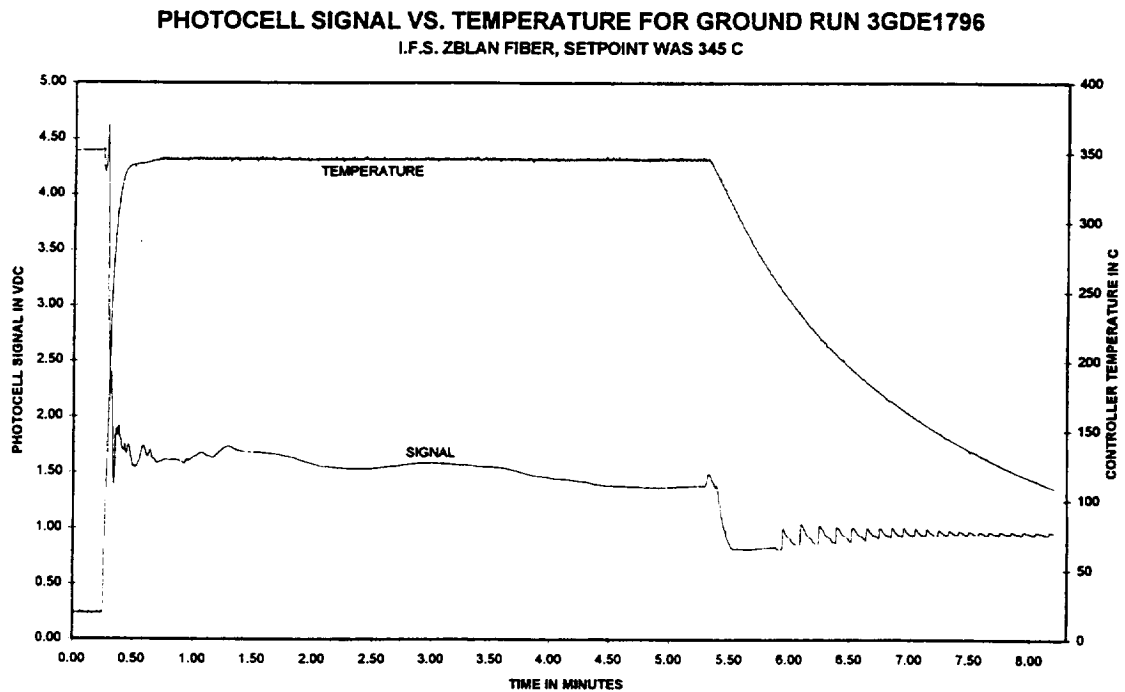


Figure 32.

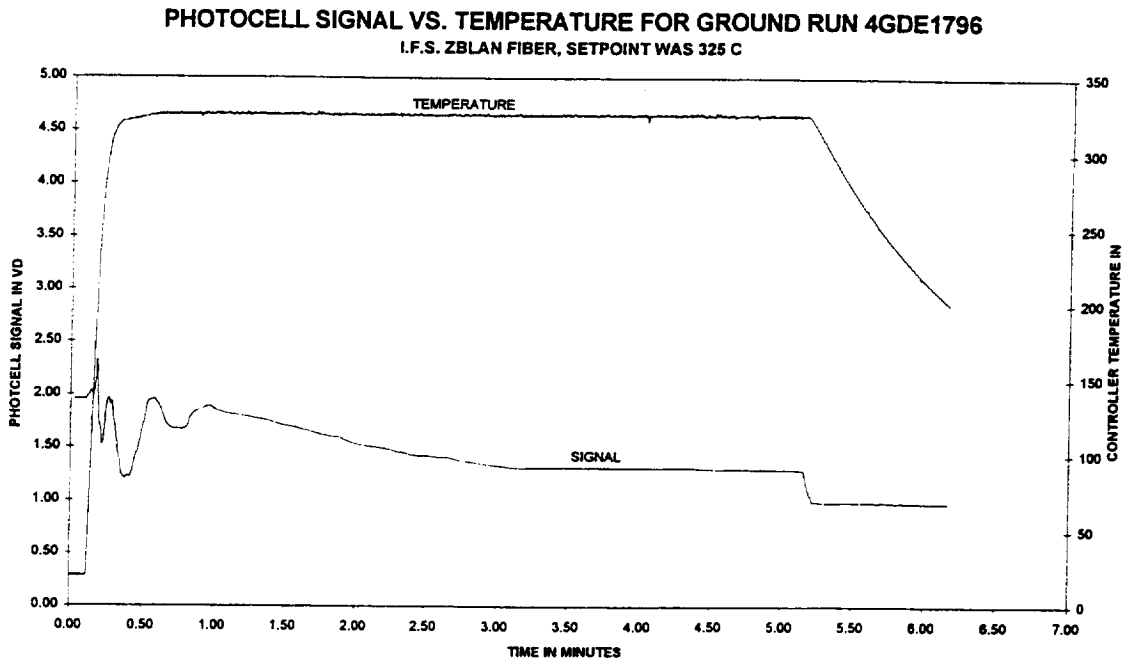
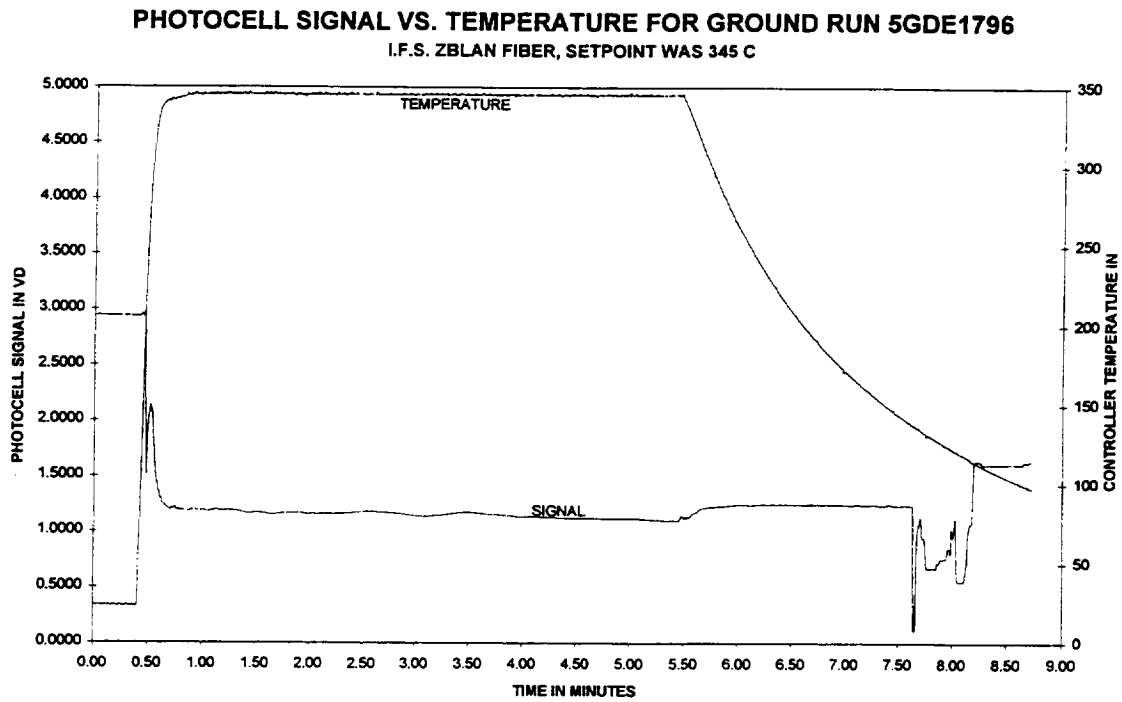


Figure 33.



3.0 Conclusions

However, the preliminary results suggest that disks of ZBLAN may be more useful sample format for the experiment. Some conceptual design is still necessary to develop the hardware to preheat just below the glass transition temperature and rapidly heat up the sample to above the crystallization temperature for the 20 seconds of low g on the KC-135. A full field of view camera system may also be more useful for picking out the distribution of the nucleation events.

Although DSC and DTA are quite useful for studying phase transformations in glass materials, they currently are measureable only on earth due to the constraints of the instrumentation. An equally sensitive method, that is applicable to microgravity processing, is the use of laser scattering to probe bulk ZBLAN and other fluorozirconates to study the kinetics of crystallite formation in these materials. A sounding rocket experiment may also be more fruitful.

A major difficulty associated with microgravity experiments is to find a method of quantifying nucleation and growth that is compatible with operational characteristics in space. DSC and DTA are certainly not currently available as tools to use in space. Laser light scattering is certainly quantifiable and space hardware is available through the microgravity sciences program.

Several studies have been performed to determine rate constants for nucleation and growth in HMFG on earth. Performing the same experiments in microgravity would allow us to evaluate the effect of gravity on the process and to obtain a better understanding of how HMFG behave differently from other types of glasses. The laser scattering experiments do provide a sensitive measure of the nucleation and growth events occurring in a transparent material. For rapid determination of the distribution of the precipitated particles. A full field of view camera is probably more appropriate arranged in a back scatter mode. We intend to work with this concept. Heating the sample above T_g is still an important consideration for KC-135 experiments since 20 seconds of low g is all you get. We are currently considering radiant heating rather than the kanthal furnace used in the prior KC-135 experiments.

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27. "Defects in Zirconium Fluoride Glasses", F. Gan, Q. Chen, and R. Lea, *Mats. Sci. Forum* vols **32-33** (1988) pp. 237-242

Although DSC and DTA are quite useful for studying phase transformations in glass materials, they currently are measureable only on earth due to the constraints of the instrumentation. An equally sensitive method, that is applicable to microgravity processing, is the use of laser scattering to probe bulk ZBLAN and other fluorozirconates to study the kinetics of crystallite formation in these materials.

A major difficulty associated with microgravity experiments is to find a method of quantifying nucleation and growth that is compatible with operational characteristics in space. DSC and DTA are certainly not currently available as tools to use in space. Laser light scattering is certainly quantifiable and space hardware is available through the microgravity sciences program.

Several studies have been performed to determine rate constants for nucleation and growth in HMFG on earth. Performing the same experiments in microgravity would allow us to evaluate the effect of gravity on the process and to obtain a better understanding of how HMFG behave differently from other types of glasses. The laser scattering experiments do provide a sensitive measure of the nucleation and growth events occurring in a transparent material. For rapid determination of the distribution of the precipitated particles. A full field of view camera is probably more appropriate arranged in a back scatter mode. We intend to work with this concept. Heating the sample above T_g is still an important consideration for KC-135 experiments since 20 seconds of low g is all you get. We are currently considering radiant heating rather than the kanthal furnace used in the prior KC-135 experiments.

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Report Document Page

1. Report No.		2. Government Accession No.		3. Recipients Catalog No.	
4. Title and Subtitle ZBLAN Phase B Study		5. Report Due			
		6. Performing Organization Code University of Alabama in Huntsville			
7. Author(s) G. L. Workman, G A. Smith, S. O'Brien		8. Performing Organization Report No.			
		10. Work Unit. No.			
9. Performing Organization Name and Address University of Alabama in Huntsville Huntsville, Alabama 35899		Contract or Grant No. NAS8-38609 D.O. 165			
		13. Type of report and Period covered Draft Final			
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-001 Marshall Space Flight Center, AL 35812		14. Sponsoring Agency Code			
		15. Supplementary Notes			
16. Abstract A Phase B feasibility study will be performed for the study of the effects of microgravity on the preform processing and fiber pulling of ZBLAN optical glass. Continuing from the positive results achieved in the fiber annealing experiments in 20 second intervals at 0.001g on the KC-135 and the 5 minute experiments on the SPAR rocket, experiments will continue to work towards design of a fiber sting to initiate fiber pulling operations in space. Anticipated results include less homogeneous nucleation than ground-based annealed fibers. Infrared Fiber Systems and Galileo are the participating industrial investigators.					
17. Key Words (Suggested by Author (s)) Microgravity Materials Processing Optical Fibers, Rocket Experiments			18. Distribution Statement cc:		
			LA10 <1> EM11/D. Hipp <1> ONRR <1> EH34/D. Tucker <1 + repro.> NASA/CASI <1 + repro.> CN22D <3> Schroer/UAH <1>		
19. Security Class. (of this report) Unclassified		20. Security Class. (of this page) Unclassified		21. No. of pages	
				22. Price	